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(71) Applicants *(for all designated States except US)*: **IBULE PHOTONICS INC.** [KR/KR]; #1276-10, Jeong-wang-dong, Siheung-si, Kyungki-do 429-850 (KR). **EUN, Jaehwan** [KR/KR]; #112-14, Hyoja-1-dong, Wansan-gu, Jeonju-si, Jeonrabuk-do 560-241 (KR). **LEE, Sang-Goo** [KR/KR]; Jugong 5-cha Apt. 508-305, #1844, Jeong-wang-dong, Siheung-si, Kyungki-do 429-450 (KR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **KIM, Hyeongjoon** [KR/KR]; Parktown 107-1303, Naejeong-dong, Bundang-gu, Seongnam-si, Kyungki-do 463-808 (KR). **KIM, Minchan** [KR/KR]; Woosung Apt. 204-502, #113-6, Ildo-2-dong, Jeju-si, Jeju-do 690-012 (KR).

(74) Agents: **JANG, Seongku** et al.; 19th Fl., KEC Building, 275-7, Yangjae-dong, Seocho-ku, Seoul 137-130 (KR).

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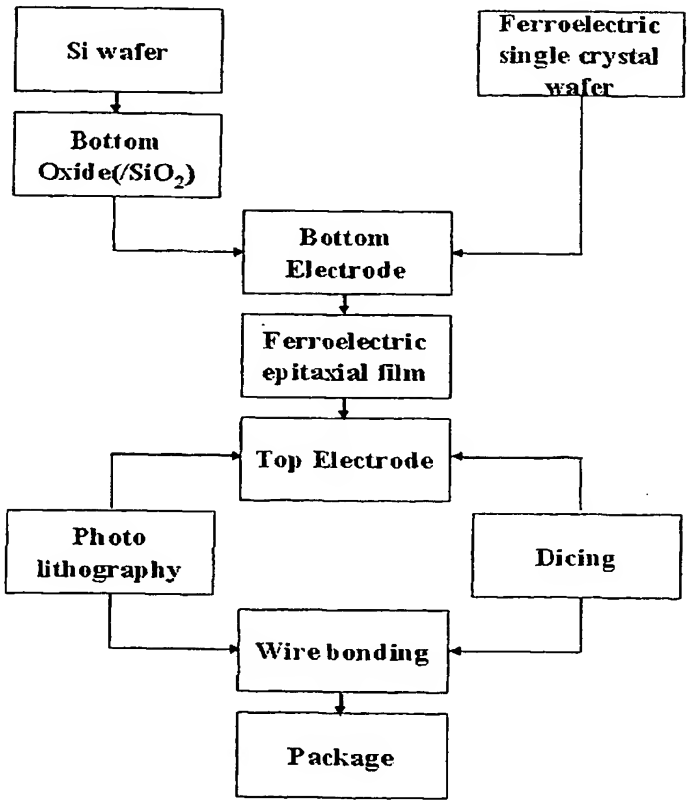
(54) Title: METHOD FOR PREPARATION OF FERROELECTRIC SINGLE CRYSTAL FILM STRUCTURE USING DEPOSITION METHOD



(57) Abstract: A film structure of a ferroelectric single crystal which can be beneficially used in the fabrication of high-performance electric and electronic parts and devices is prepared by forming an electrode layer having a perovskite crystal structure on a substrate made of a silicon or ferroelectric single crystal optionally polished to have a off-axis crystal structure, and epitaxially growing a layer of a ferroelectric single crystal thereon by pulsed laser deposition (PLD) or metallorganic chemical vapor deposition (MOCVD).

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METHOD FOR PREPARATION OF FERROELECTRIC SINGLE CRYSTAL FILM STRUCTURE USING DEPOSITION METHOD

Field of the Invention

The present invention relates to a method for preparing a film structure comprising a ferroelectric single crystal, useful for the fabrication of many electric and electronic devices, particularly by way of employing a pulsed laser deposition (PLD) or metallorganic chemical vapor deposition (MOCVD).

Background of the Invention

A ferroelectric thin film or thick film is frequently used in various electric and electronic parts, and it has been hitherto prepared by coating a PZT film on a substrate by a screen-printing or sol-gel method, calcining the coated substrate to crystallize the material, or by depositing the single crystal-forming raw material under a vacuum (see N. Setter, Piezoelectric Materials in Devices, Ceramics Laboratory, EPFL 2002).

Although the prior methods are simple and convenient, the film thus prepared still exhibits unsatisfactory performance characteristics in terms of current loss, electromechanical coupling coefficient and dielectric constant. Further, the calcination step of the prior methods requires the use of a high-cost, high-melting metal such as Pt and Au as an electrode material.

Therefore, there has existed a need to develop a simple method of providing a ferroelectric film, especially in the form of a single crystal layer, of improved properties suitable for electric and electronic devices and parts.

Summary of the Invention

It is, therefore, a primary object of the invention to provide a novel method for preparing a ferroelectric film structure using a ferroelectric single crystal having a high dielectric constant together with good electromechanical and electrooptical properties.

In accordance with an aspect of the present invention, there is provided a method for preparing a film structure of a ferroelectric single crystal, which comprises forming a layer of an electrode material having a perovskite crystal structure on a substrate, and growing a layer of a ferroelectric single crystal on the electrode material layer by a pulsed laser deposition (PLD) or metallorganic chemical vapor deposition (MOCVD) method.

Brief Description of the Drawings

The above and other objects and features of the present invention will become apparent from the following description thereof, when taken in conjunction with the accompanying drawings which respectively show:

Fig. 1: a schematic block diagram of the process for preparing a single crystal film structure according to the present invention;

Fig. 2a to 2e: the procedure for preparing a ferroelectric single crystal film structure using a silicon single crystal substrate having an on-axis crystal structure; and

Fig. 3a to 3e: the procedure for preparing a ferroelectric single crystal film structure using a ferroelectric single crystal substrate having an off-axis crystal structure.

Detailed Description of the Invention

The inventive method for preparing a ferroelectric film structure is

characterized by epitaxially growing a ferroelectric single crystal layer on an electrode material layer having a perovskite crystal structure via a PLD or MOCVD method. Preferably, in the inventive method, a silicon or ferroelectric single crystal plate optionally polished to have off-axis crystal structure may be used as a substrate, and in the case of using silicon substrate, a metal oxide layer having a perovskite crystal structure may be further introduced before the formation of the electrode layer as an intermediate layer between the substrate and the electrode layer.

In the present invention, a ferroelectric single crystal material having a dielectric constant of 1,000 or higher as measured in the form of a film may be preferably employed.

Representative examples of the ferroelectric single crystal used in the present invention include PMN-PT (lead magnesium niobate-lead titanate), PZN-PT (lead zinc niobate-lead titanate), LN (lithium niobate, $LiNbO_3$), LT (Lithium tanthalate, $LiTaO_3$), langasite($La_3Ga_5SiO_{14}$) and other piezoelectric and electrooptical materials known in the art.

The PMN-PT- and PZN-PT-based materials preferably have the composition of formula (I):

x(A)y(B)z(C)-p(P)n(N) (I)

wherein,

(A) is $Pb(Mg_{1/3}Nb_{2/3})O_3$ or $Pb(Zn_{1/3}Nb_{2/3})O_3$,

(B) is $PbTiO_3$,

(C) is $LiTaO_3$,

(P) is a metal selected from the group consisting of Pt, Au, Ag, Pd and Rh,

(N) is an oxide of a metal selected from the group consisting of Ni, Co, Fe, Sr, Sc, Ru, Cu and Cd,

x is a number in the range of 0.65 to 0.98,

y is a number in the range of 0.01 to 0.34,

z is a number in the range of 0.01 to 0.1, and

p and n are each independently a number in the range of 0.01 to 5.

The material of formula (I) is a homogeneous single crystal and it may be prepared by a solid phase reaction followed by melting-crystallization, as disclosed in Korean Patent Laid-open Publication No. 2001-96505. Specifically, the materials of formula(I) may be prepared by (a) mixing a component selected from $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$ with $PbTiO_3$, and $LiTaO_3$, in relative molar amounts ranging from 0.65 to 0.98, 0.01 to 0.34 and 0.01 to 0.1, respectively, (b) adding to the mixture obtained in (a), a metal selected from the group consisting of Pt, Au, Ag, Pd and Rh, and an oxide of a metal selected from the group consisting of Ni, Co, Fe, Sr, Sc, Ru, Cu and Cd, in amounts ranging from 0.01 to 5 % by weight based on the mixture, (c) calcining the mixture obtained in (b), followed by pulverizing the calcination product, (d) melting the powder obtained in (c), and (e) cooling the melt to crystallize. The single crystal prepared by the above procedure preferably has a diameter of 5 cm or greater.

The LN single crystal can be prepared from Li_2CO_3 and Nb_2O_5, the LT single crystal, from Li_2CO_3 and Ta_2O_5, and the langasite single crystal, from La_2O_3, Ga_2O_3 and SiO_2, by Czochralski's method (see Yuhuan Xu, Ferroelectric materials and their applications, pp 221-224, North-holland (1991)). These materials are commercially available.

In particular, the ferroelectric single crystal of formula (I) has an electro-mechanical coupling coefficient superior to that of the existing PZT single or poly crystal as well as a high driving voltage, a wide range of bending deformation, and good electrooptical property, and thus it can be processed minutely. The ferroelectric material of formula (I) has a dielectric constant of about 7,000 (in a film form, about 2,000), a loss piezoelectric constant of about 0.001 (in a film form, about 0.003), d_{33} of about 2,500 and k_{33} of about 0.97. The existing PZT film typically

shows a dielectric constant of about 400 to 500 and a loss piezoelectric constant of about 0.006 to 0.02.

The method of preparing a single crystal film structure according to the present invention is described below with reference to the accompanying drawings.

As shown in Fig. 1, in accordance with the present invention, a single crystal film structure can be prepared by optionally forming an oxide layer having a perovskite crystal structure on a Si or ferroelectric single crystal substrate having an on-axis crystal structure or an off-axis crystal structure, forming a layer of a material having a perovskite crystal structure thereon as a bottom electrode layer, and epitaxially growing a ferroelectric single crystal layer on the electrode layer by a PLD or MODVD method. Subsequently, the single crystal film structure prepared by the inventive method may be used in the fabrication of an electronic or electric part in a conventional manner, e.g., by forming a top electrode layer on the single crystal layer, patterning the resulting laminate by etching via a photolithography or dicing, and wiring the patterned laminate.

Fig. 2a to 2e shows the procedure for preparing a ferroelectric single crystal film structure using a silicon single crystal substrate having an on-axis crystal structure, and Fig. 3a to 3e, using an off-axis ferroelectric single crystal substrate.

Fig. 2a represents an optional step of forming an oxide layer (20) on a Si substrate (10) in a conventional manner. The oxide layer (20) may be preferably formed by a PLD or MOCVD method to a thickness of 10 μm or less. The oxide layer may be formed by ALD(Atomic Laser Deposition), MBE(Molecular Beam Epitaxy) and other methods. Preferably, the oxide layer (20) may be made of a material having the same perovskite crystal structure as a ferroelectric single crystal, e.g., strontium titanate (STO; $SrTiO_3$).

Although not shown in the figure, the Si substrate (10) may be previously oxidized by heat-treatment to form a SiO_2 thin film of 1 μm thick or less thereon, before

the formation of the oxide layer (20).

Subsequently, Fig. 2b shows the step of forming a bottom electrode layer (30) on the oxide layer (20), in the same manner as described in the formation of the oxide layer(20). The bottom electrode layer (30) may be formed to a thickness of 5 μm or less, and it may be made of a material having a perovskite crystal structure similarly to the oxide layer (20) and having a specific resistance of 9×10^{-4} Ω cm or less. The bottom electrode layer (30) may be preferably made of strontium ruthenate (SRO; $SrRuO_3$) or lanthanium nickelate (LNO; $LaNiO_3$) having a specific resistance of about 1×10^{-4} to 9×10^{-4} Ω cm.

In accordance with the present invention, the formation of the bottom electrode layer and the optional oxide layer having the same perovskite crystal structure as that of the ferroelectric single crystal layer being deposited thereon can provide a seed for growing the ferroelectric single crystal.

Fig. 2c depicts the step of epitaxially growing a ferroelectric single crystal layer (40) on the bottom electrode layer (30). The epitaxial growth of the ferroelectric single crystal layer (40) may be achieved by pulsed laser deposition (PLD) in which a ferroelectric single crystal target is irradiated with a high-energy laser beam to be deposited on a substrate, or metallorganic chemical vapor deposition (MOCVD) in which an organic metal compound precursor is vaporized to be deposited on a substrate. The PLD or MOCVD may be carried our in a conventional manner as known in the art.

Representative precursors for the formation of the PMN-PT single crystal film include $Pb(THD)_2$, Mg(THD), $Nb(THD)_4$, and $Ti(THD)_2$ (THD=tetramethyl heptanedionate). Similarly, an LN film may be deposited from Li(THD) and $Nb(THD)_4$, and an LT film, Li(THD) and $Ta(THD)_4$.

The single crystal layer (40) may be suitably formed to a thickness ranging from 0.1 to 20 μm.

The single crystal film structure according to the present invention thus prepared

may be further processed for the fabrication of various electric or electronic parts or devices. Fig. 2d represents the step of forming a top electrode (50) on the ferroelectric single crystal layer (40) by a conventional method, e.g., using a sputtering or electron beam evaporation method. In the prior art method in which a PZT paste is screen-printed and then calcined at 1,000 ℃ or higher to form a polycrystalline thin film, an expensive metal such as Pt, Au and Ag having a high melting temperature must be used as the top electrode. In the present invention, however, an inexpensive material including Al may be used. The thickness of the top electrode (50) may range from about 1 to 5 μm.

Subsequently, the step of polarizing the ferroelectric single crystal layer (40) disposed between the top and bottom electrodes (30 and 50) to obtain a polarized single crystal layer (40a) is shown in Fig. 2e. The polarizing process can be conducted by applying an electric field of 10 to 100 kV/cm to the single crystal layer (40) at 100 to 300 ℃ for 10 to 100 minutes.

Fig. 3a shows the step of making an off-axis ferroelectric single crystal substrate (110a) having an off-axis angle of 0.1 to 10°, from a single crystal substrate (110) having a crystallinity oriented along the C (vertical) axis, by polishing. In general, the growth of a single crystal occurs more easily in the lateral direction than the perpendicular direction with respect to the crystal plane. Since the above polishing process generates stairs of seed portions for growing the single crystal, it may facilitate the epitaxial growth of the ferroelectric single crystal via deposition.

Fig. 3b shows the step of forming a bottom electrode layer (130) on the single crystal substrate (110a), and Fig. 3c depicts the step of forming a ferroelectric single crystal layer (140) on the bottom electrode layer (130). Further, Fig. 3d represents the step of forming a top electrode (150) and Fig. 3e shows the step of polarizing the ferroelectric single crystal layer (140). The above steps may be carried out in the same manner as described previously in Fig. 2b to Fig. 2e.

The laminates shown in Fig. 2e and Fig. 3e may be beneficially used in the fabrication of various electric or electronic parts and devices including a microactuator, an ultrasonic probe, a variable filter, and the like by etching or dicing the laminate via a photolithography to form a pattern thereon and wiring the patterned laminate.

While the invention has been described in connection with the above specific embodiments, it should be recognized that various modifications and changes may be made to the invention by those skilled in the art without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. A method for preparing a film structure of a ferroelectric single crystal, which comprises the steps of: forming a layer of a material having a perovskite crystal structure on a substrate as an electrode layer, and growing a layer of a ferroelectric single crystal on the electrode material layer by a pulsed laser deposition (PLD) or metallorganic chemical vapor deposition (MOCVD) method.

2. The method of claim 1, wherein the grown ferroelectric single crystal layer has a thickness of 0.1 to 20 μm.

3. The method of claim 1, wherein the substrate is made of a silicon single crystal or a ferroelectric single crystal.

4. The method of claim 1, which further comprises polishing the single crystal substrate to form a single crystal substrate having an off-axed crystal structure

5. The method of claim 4, wherein the single crystal substrate has an off-axis angle of 0.1 to 10° with respect to the C axis.

6. The method of claim 1, wherein the electrode layer having the perovskite crystal structure is made of strontium ruthenate ($SrRuO_3$) or lanthanium nickelate($LaNiO_3$).

7. The method of claim 1, wherein the electrode layer has a specific resistance of 9×10^{-4} Ω cm or less.

8. The method of claim 1, which further comprises forming a metal oxide layer having a perovskite crystal structure on the substrate before the formation of the electrode layer.

9. The method of claim 8, wherein the metal oxide layer having the perovskite crystal structure is made of strontium titanate ($SrTiO_3$).

10. The method of claim 1 or 8, wherein the electrode or metal oxide layer is formed by a PLD or MOCVD method.

11. The method of claim 1, wherein the ferroelectric single crystal has a dielectric constant of 1,000 or greater as measured in a film form.

12. The method of claim 1, wherein the ferroelectric single crystal is $LiNbO_3$, $LiTaO_3$, $La_3Ga_5SiO_{14}$ or a material having the composition of formula (I):

x(A)y(B)z(C)-p(P)n(N) (I)

wherein,

(A) is $Pb(Mg_{1/3}Nb_{2/3})O_3$ or $Pb(Zn_{1/3}Nb_{2/3})O_3$,

(B) is $PbTiO_3$,

(C) is $LiTaO_3$,

(P) is a metal selected from the group consisting of Pt, Au, Ag, Pd and Rh,

(N) is an oxide of a metal selected from the group consisting of Ni, Co, Fe, Sr, Sc, Ru, Cu and Cd,

x is a number in the range of 0.65 to 0.98,

y is a number in the range of 0.01 to 0.34,

z is a number in the range of 0.01 to 0.1, and

p and n are each independently a number in the range of 0.01 to 5.

13. The method of claim 1, which further comprises forming a conductive metal layer on the surface of the ferroelectric single crystal layer opposite to the electrode layer having the perovskite crystal structure, by a sputtering or an electronic beam evaporation method.

14. The method of claim 1, which further comprises oxidizing the substrate by heat-treatment to form a thin oxide film of 1 μm or less on the substrate.

15. A ferroelectric single crystal film structure prepared by a method according to any one of claims 1 to 14.

16. An electric or electronic device comprising the ferroelectric single crystal film structure according to claim 15.

Fig. 1

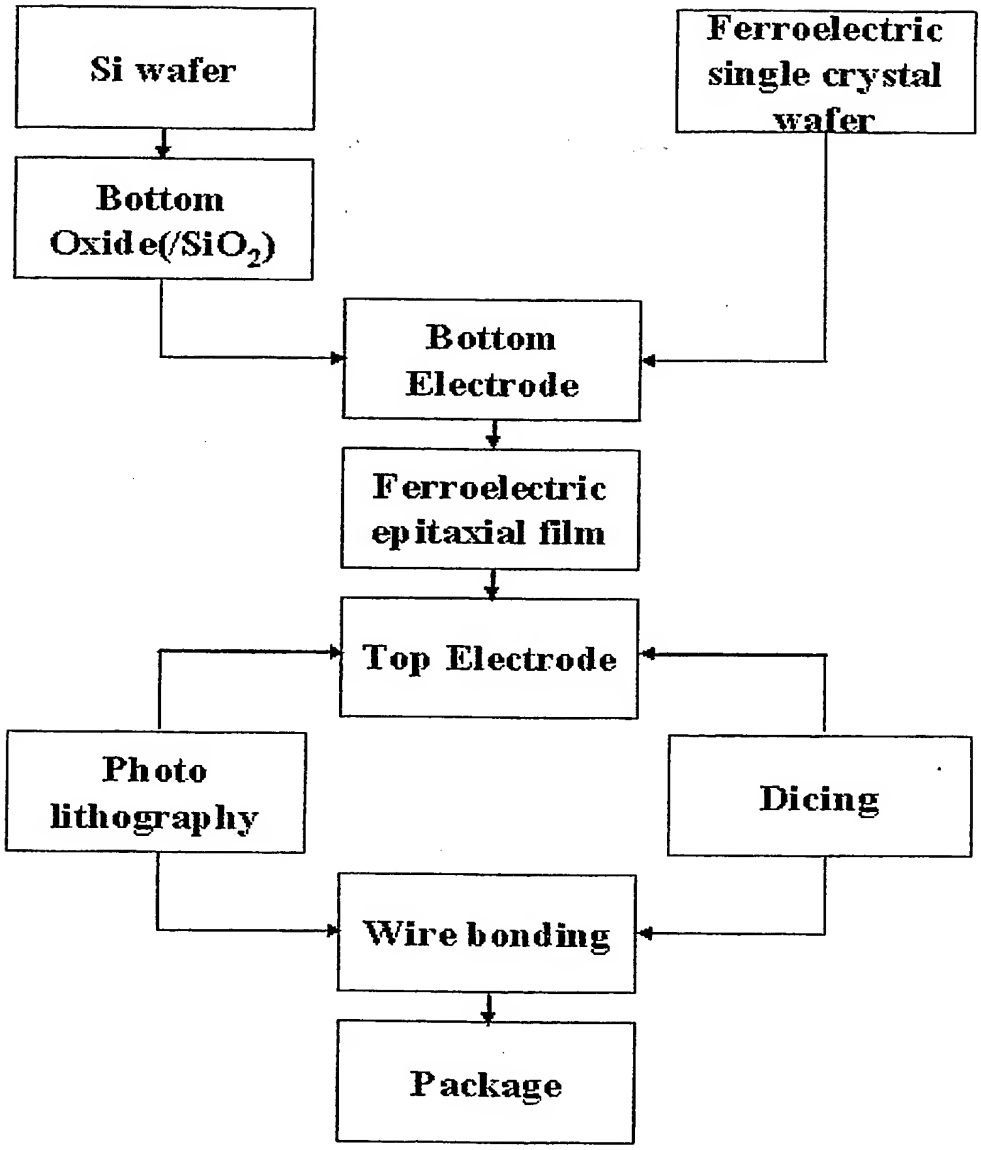

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Fig. 2a

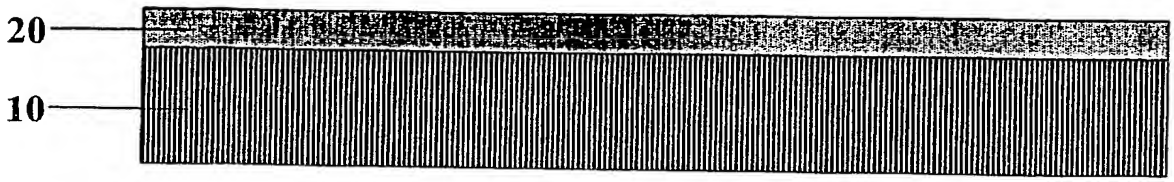


Fig. 2b

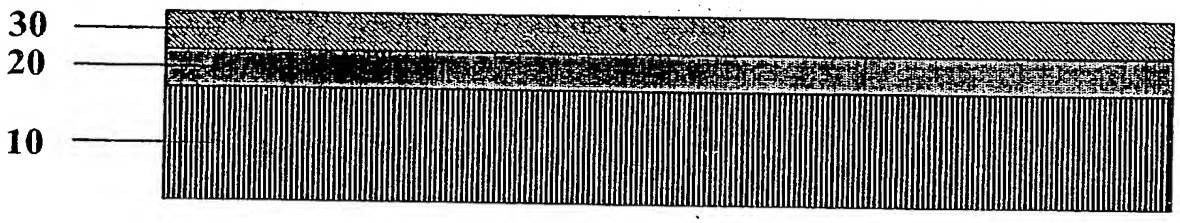


Fig. 2c

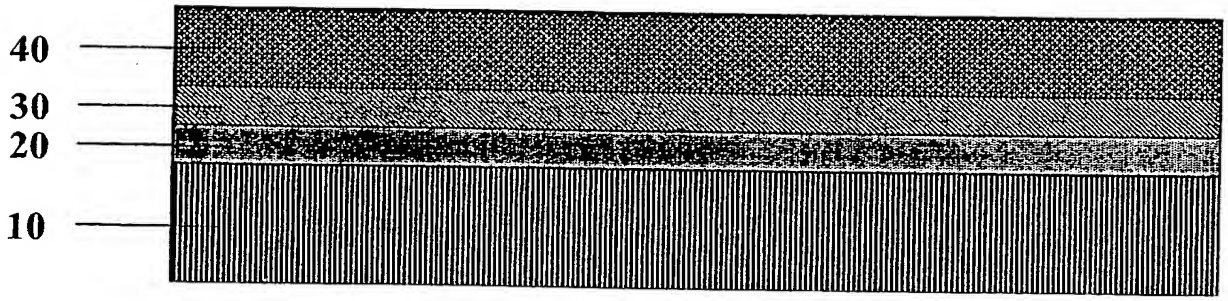


Fig. 2d

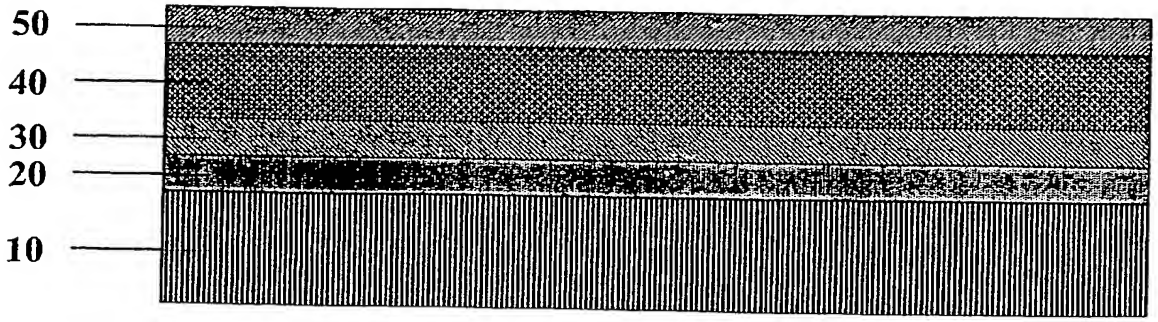


Fig. 2e

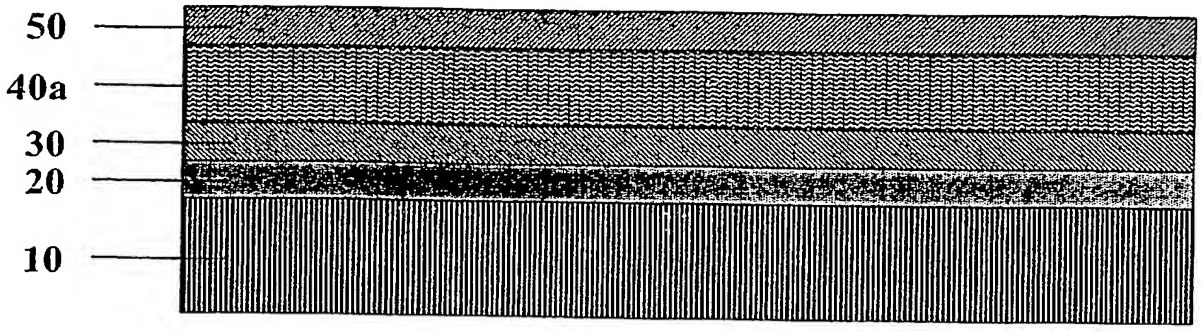


Fig. 3a

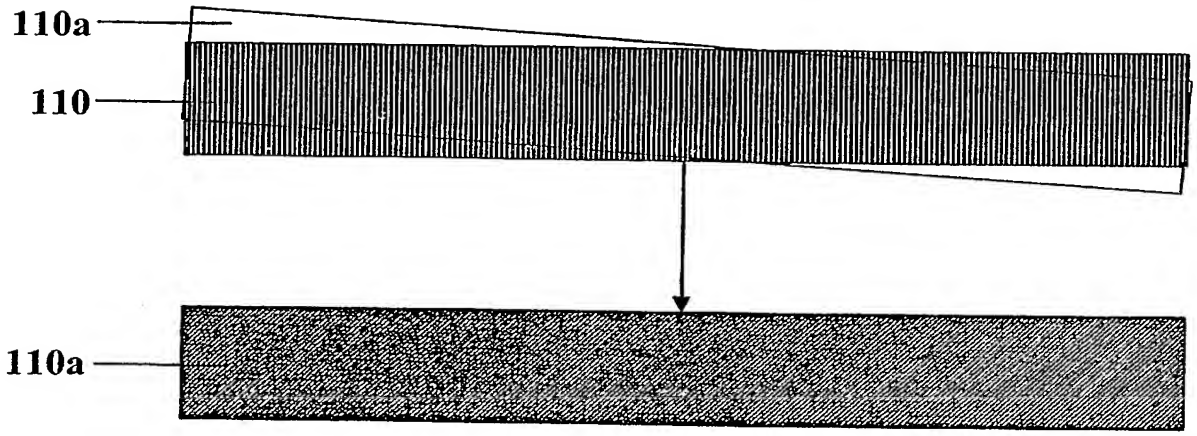


Fig. 3b

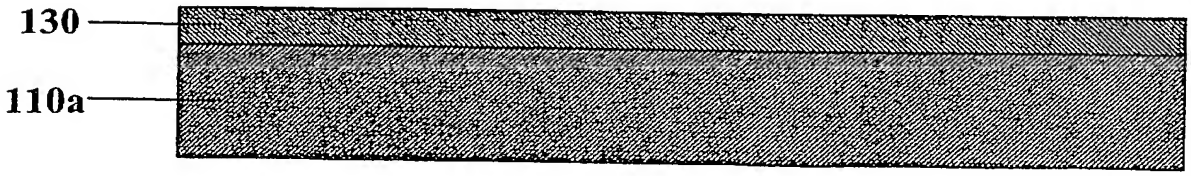


Fig. 3c

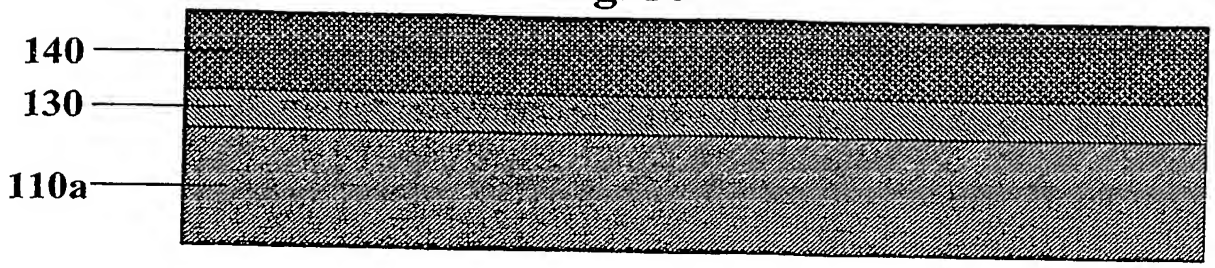


Fig. 3d

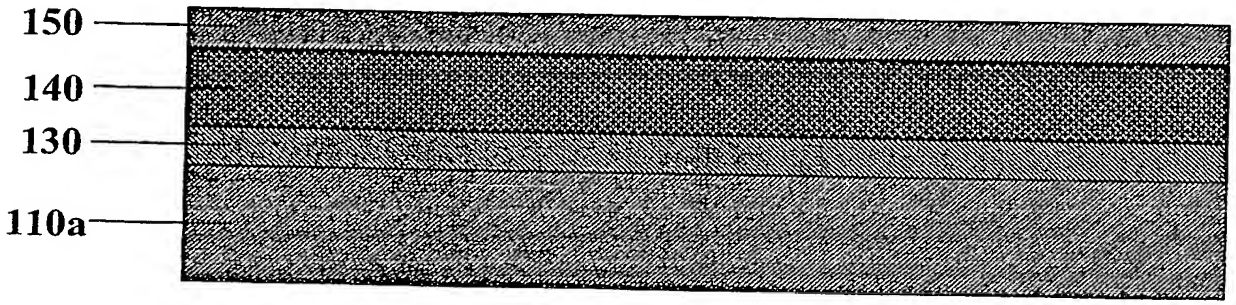
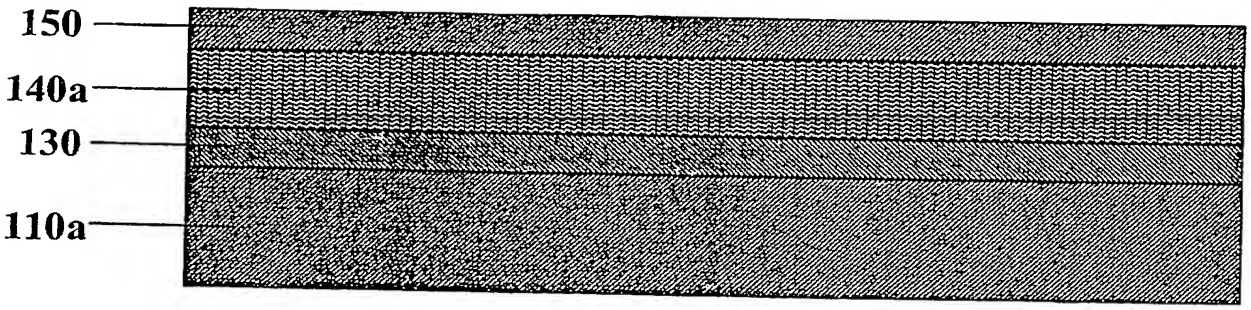


Fig. 3e



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR03/01391

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 H01L 21/205

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC7 H01L21/20, H01L21/02, C23C16/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
KOREAN PATENTS AND APPLIACTIONS FOR INVENTIONS SINCE 1975
KOREAN UTILITY MODELS AND APPLICATIONS FOR UTILITY MODELS SINCE 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
KIPONET

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 12-068455 A (NEC CORP) 03.MARCH. 2000 Abstract, figure 1 and description	1, 11
Y	JP 09-186376 A (SHARP CORP) 15. JURY. 1997 See the whole document	1, 11
Y	US 6054331 B (DONG YANG CEMENT CORP) 25. APRIL. 2000 Claim 1, Abstract	1, 11
A	KR 1998-80778 A(CANON CORP) 25. NOVEMBER. 1998. Abstract and Claim1	1, 2, 3, 8
Y	JP 08-253324 A (SUMITOMO METAL MINING CO.,LTD) 01.OCTOBER.1996 See the whole document	1, 3, 4, 8, 10, 11
A	JP13-107238 A (SHARP CORP) 17. APRIL. 2001 Abstract and Claim1	1, 3, 4, 8, 10, 11

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
29 OCTOBER 2003 (29.10.2003)	30 OCTOBER 2003 (30.10.2003)
Name and mailing address of the ISA/KR Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer LEE, Son Taek Telephone No. 82-42-481-5980

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR03/01391

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 05650362 B (FUJI XEROX CO.,LTD) 22. JULY. 1997 Abstract and all Claims	1, 2, 3, 8, 10, 11
A	US 6498097 B (DONG YANG CEMENT CO.,LTD) 24. DECEMBER.2002 See the whole document	1 - 11
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
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